1
2   **NANOSTRUCTURED CHEMICALS AS ALLOYING AGENTS
        IN FLUORINATED POLYMERS**
3

4   **Cross-Reference to Related Applications**

5   This application claims the benefit of U.S. Provisional Application No. 60/459,357 filed

6   on March 31, 2003, and is a continuation-in-part of U.S. Patent Application No. 09/818,265 filed

7   March 26, 2001, which claims the benefit of U.S. Provisional Application No. 60/192,083, filed

8   March 24, 2000.

9

10   **Field of the Invention**

11   This invention relates generally to methods for enhancing the properties of thermoplastic

12   and thermoset fluorinated polymer and fluid compositions and, more particularly, to methods for

13   the incorporation of nanostructured chemicals into fluorinated polymers and fluorinated fluids.

14   This invention also relates to several applications of the fluorinated polymers with

15   improved properties. These applications include space-survivable materials and creep resistant

16   seals and gaskets. Improved polymer surface properties may be useful for applications such as

17   anti-icing or non-wetting surfaces or as low friction surfaces.

18

19   **BACKGROUND OF THE INVENTION**

20   It has long been recognized that the properties of polymers can be tailored to a high

21   degree through variables such as polymer sequence, structure, additive and filler incorporation,

22   composition, morphology, thermodynamic and kinetic processing control. It is similarly known

23   that various sizes and shapes of fillers, and particulates (e.g. calcium carbonate, silica, carbon

1 black etc.) can be incorporated into preformed polymers or prepolymers or monomer mixtures to

2 enhance physical and material properties of the resulting formulations.

3   In their solid state all polymers (including amorphous, semi-crystalline, crystalline, and

4 rubber, etc.) possess considerable amounts of internal and external free volume (see Figure 1).

5 The free volume of a polymer has a tremendous impact on its physical properties, since it is

6 within this volume that the dynamic properties (e.g. reptation, translation, rotation,

7 crystallization) of polymer chains primarily operate and in turn influence fundamental physical

8 properties such as density, thermal conductivity, glass transition, melt transition, modulus,

9 relaxation, and stress transfer.

10   The accessibility of free volume in a polymer system depends greatly on its morphology

11 and on the size of the agent desired to occupy the free volume. As shown in Figure 2, for

12 example, denser regions and phase separation within a polymer can both increase and decrease

13 the thermodynamic and kinetic access to such areas. Because of its influence on thermodynamic

14 and kinetic properties, polymer morphology and free volume dimension are major factors that

15 limit the ability of conventional fillers from accessing the free volume regions in a polymer

16 system. Additional processing/compounding effort is normally required to force

17 compatibilization between a filler and a polymer system because conventional fillers are

18 physically larger than most polymer dimensions, are chemically dissimilar, and usually are high

19 melting solids.

20   Prior art in fluoropolymers has focused on modifications through the formation of an

21 inorganic interpenetrating network that is either partially or fully condensed and is in contact

22 with or dispersed amoungst the fluoropolymer chains. See U.S. Pat. Nos. 5,876,686 and

1   5,726,247.   Similarily modifications have been described that enhance properties through the

2   continuous or discontinuous dispersion of macro, micro and nanoscale particulates of a dissimilar

3   composition (e.g. inorganic) relative to that of the fluoropolymer. In either case the function of

4   the inorganic network or filler particle is to reduce the relative slippage or motion of the

5   fluoropolymer chains and segments relative to each other. The combination of reduced chain

6   motion with the thermally stable inorganic component utlimately enhances physical properties

7   such as dimensional stability, impact resistance, tensile and compressive strengths, thermal

8   stability, electrical properties, abrasion and chemical resistance, shrinkage and expansion

9   reduction. Unfortunately, all of the prior art either suffers from process complexity, a length

10   scale of the reinforcement that is too large to sufficiently access polymer free volume, or

11   reinforcement that lacks sufficient geometrical definition to provide structure regularity and

12   reinforcement at the molecular (10^{-10} m) and nanoscopic (10^{-9} m) length scales. As illustrated in

13   Figure 4, fillers are geometrically ill defined solid particulates that macroscopically or

14   nanoscopically reinforce large associated or nearby groups of polymers rather than the individual

15   chains and segments within these polymers. As illustrated in Figure 5, incompletely condensed

16   or completely condensed interpenetrating networks also lack sufficient geometrical definition to

17   provide structure regularity and reinforcement of fluoropolymer chains.

18   Furthermore, it has been calculated that as filler sizes decrease below 50nm, they would

19   become more resistant to sedimentation and more effective at providing reinforcement to

20   polymer systems. The full application of this theoretical knowledge, however, has been thwarted

21   by the lack of a practical source of particulate reinforcement or reinforcements which are

22   geometrically well defined, and monodisperse and with diameters below the 10 nm range and

23   especially within the 1 nm to 5 nm range.   Particularly desirable are monodisperse,

1 nanoscopically sized chemicals with precise chemical compositions, rigid and well defined

2 geometrical shapes, and which are dimensionally large enough to provide reinforcement of

3 polymer chains. Such nanoscopic chemicals are desirable as they are expected to form the most

4 stable dispersions within polymer systems, would be well below the length scale necessary to

5 scatter light and hence are visually nondetectable when incorporated into fluoropolymers, and

6 would be chemically compatible with fluoropolymers and dissolve into and among the polymer

7 chains, thus eliminating the need for extensive dispersion or reactive self assembly or the

8 complex processing requirements of the prior art.

9 Recent developments in nanoscience have enabled the ability to cost effectively

10 manufacture commercial quantities of materials that are best described as nanostructured

11 chemicals due to their specific and precise chemical formula, hybrid (inorganic-organic)

12 chemical composition, large physical size relative to the size of traditional chemical molecules

13 (0.3-0.5nm), and small physical size relative to larger sized traditional fillers (>50nm).

14 Nanostructured chemicals are best exemplified by those based on low-cost Polyhedral

15 Oligomeric Silsesquioxanes (POSS) and Polyhedral Oligomeric Silicates (POS). Figure 3

16 illustrates some representative examples of monodisperse nanostructured chemicals, which are

17 also known as POSS Molecular Silicas.

18 These systems contain hybrid (i.e., organic-inorganic) compositions in which the internal

19 frameworks are primarily comprised of inorganic silicon-oxygen bonds. The exterior of a

20 nanostructure is covered by both reactive and nonreactive organic functionalities (R), which

21 ensure compatibility and tailorability of the nanostructure with organic polymers. These and

22 other properties of nanostructured chemicals are discussed in detail in U.S. Pat. Nos. 5,412,053

23 and 5,484,867, both are expressly incorporated herein by reference in their entirety. These

1   nanostructured chemicals are of low density, exhibit excellent inherent fire retardancy, and can

2   range in diameter from 0.5nm to 5.0nm.

3   Prior art associated with fillers, plasticizers, interpenetrating networks, and polymer

4   morphology has not been able to adequately control polymer chain, coil and segmental motion at

5   the 1nm-10nm level. Furthermore, the mismatch of chemical potential (e.g., solubility,

6   miscibility, etc.) between fluoro-based polymers and inorganic-based fillers and chemicals results

7   in a high level of heterogeneity in compounded polymers that is akin to oil mixed with water.

8   Therefore, there exists a need for appropriately sized chemical reinforcements for polymer

9   systems with controlled diameters (nanodimensions), distributions and with tailorable chemical

10 functionality.   In   addition,   it   would   be   desirable   to   have   easily   compoundable

11 nanoreinforcements that have chemical potential ranges (misibilities) similar to the various

12 fluorinated polymer and fluorinated fluid systems.

13

14   **SUMMARY OF THE INVENTION**

15   The present invention describes methods of preparing new polymer compositions by

16 incorporating nanostructured chemicals into polymers. The resulting nano-alloyed polymers are

17 wholly useful by themselves or in combination with other polymers or in combination with

18 macroscopic reinforcements such as fiber, clay, glass mineral and other fillers. The nano-alloyed

19 polymers are particularly useful for producing polymeric compositions with desirable physical

20 properties such as adhesion to polymeric, composite and metal surfaces, water repellency,

21 reduced melt viscosity, low dielectric constant, resistance to abrasion and fire, biological

22 compatibility, and optical quality plastics. The preferred compositions presented herein contain

23 two primary material combinations: (1) nanostructured chemicals, nanostructured oligomers, or

1   nanostructured polymers from the chemical classes of polyhedral oligomeric silsesquioxanes,

2   polysilsesquioxanes, polyhedral oligomeric silicates, polysilicates, polyoxometallates,

3   carboranes, boranes, and polymorphs of carbon; and (2) fluorinated polymer systems such as:

4   PFA, MFA, PVDF, semicrystalline, crystalline, glassey, elastomeric, oils, and lubricants thereof

5   as derived from hydrocarbons, or silicones and fluoropolymers or copolymers thereof.

6   Preferably, the method of incorporating nanostructured chemicals into such

7   fluoropolymers is accomplished via blending of the chemicals into the polymers. All types and

8   techniques of blending, including melt blending, dry blending, solution blending, reactive and

9   nonreactive blending are effective.

10   In addition, selective incorporation of a nanostructured chemical into a specific region of

11   a polymer can be accomplished by compounding into the polymer a nanostructured chemical

12   with a chemical potential (miscibility) compatible with the chemical potential of the region

13   within the polymer to be alloyed. Because of their chemical nature, nanostructured chemicals

14   can be tailored to show compatibility or incompatibility with selected sequences and segments

15   within polymer chains and coils. Their physical size in combination with their tailorable

16   compatibility enables nanostructured chemicals to be selectively incorporated into fluoroplastics

17   and control the dynamics of coils, blocks, domains, and segments, and subsequently favorably

18   impact a multitude of physical properties. Properties most favorably improved are time

19   dependent mechanical and thermal properties such as heat distortion, creep, compression set,

20   shrinkage, modulus, hardness and abrasion resistance. In addition to mechanical properties,

21   other physical properties are favorably improved, including lower thermal conductivity,

1 improved fire resistance, and improved oxygen permeability, improved oxidative stability,

2 improved electrical properties and printability.

3 **Creep resistant seals and gaskets**

4   While many fluoropolymers, such as polytetrafluoroethylene (PTFE or Teflon) and

5 fluorinated ethylene/propylene (FEP) are resistant to organic fuels and fluids, creep is often a

6 problem. Creep is the change in dimensions of a molded part resulting from cold flow incurred

7 by continual loading and can cause a polymer press-fit to loosen to an unacceptable condition or

8 even fail. Tensile strength is an important factor in controlling the amount of cold flow in

9 plastics. The higher the tensile strength, the more resistant the plastic is to cold flow and creep.

10 PTFE, for example, has a very low tensile strength. In addition to improving thermal and

11 mechanical properties of fluoropolymers, blended fluorinated POSS reduces the amount of

12 creep. The processing temperature of nearly all fluoropolymers is sufficient to allow the

13 blending of POSS materials. A notable exception is PTFE. While the processing temperature of

14 PTFE is too high to allow conventional blending, supercritical methods may allow fluorinated

15 POSS to be incorporated into PTFE.

16

17 **Space-survivable fluorinated materials**

18   Fluorinated POSS can be blended into several fluoropolymers, including

19 poly(vinylidinefluoride) (PVDF) and FEP, both of which are used in spacecraft coatings. These

20 compounds significantly improve oxidation resistance due to a rapidly forming ceramic-like,

21 passivating and self-healing silica layer when exposed to high incident fluxes of atomic oxygen

22 (AO). AO is the predominant species in low earth orbit (LEO) responsible for material

1   degradation. This is because the collision energy of AO (~ 5 eV) exceeds the bond strength of

2   carbon-carbon bonds in fluoropolymers (~ 4.3 eV). The silicon-oxygen bonds present in the

3   POSS cage have stronger bond dissociation energies (~ 8.3 eV). The POSS cage is not destroyed

4   by the AO, but forms a passivating self-rigidizing/self-healing silica layer, which protects the

5   underlying virgin polymer.

6   **Anti-icing or non-wetting applications**

7   Fluorinated POSS films show remarkable surface properties. The contact angle of water

8   on a spin-cast surface of fluorodecyl POSS is 140° in an unoptimized process. Surprisingly, this

9   is 30 degrees higher than PTFE. A higher the contact angle indicates lower surface energy.

10   These fluorinated POSS compounds have the potential to form ultrahydrophobic surfaces and

11   also reduce the surface energy of the fluoropolymers into which they are blended. This also leads

12   to increased abrasion resistance and lubricity. Anti-icing or non-wetting applications may be

13   possible using this technology. Lubricants and low friction surfaces can also be developed.

14   These surfaces would be further enhanced by the creep reduction mentioned above.

15

16   **BRIEF DESCRIPTION OF THE DRAWINGS**

17   FIG. 1 shows the relative positions of an internal free volume and an external free volume

18   of a polymer.

19   FIG. 2 illustrates some different regions and phase separation within a polymer.

20   FIG. 3 illustrates some representative examples of monodisperse nanostructured

21   chemicals.

22   FIG. 4 illustrates the macroscopic reinforcement a traditional filler provides to polymers.

1   FIG. 5 illustrates the lack of geometrical definition of interpenetrating network polymers.

2   FIG. 6 illustrates a nanoreinforced polymer microstructure.

3   FIG. 7 is a graph of storage modulus (E*) relative to temperature (°C) for nonreinforced

4 fluoropolymer and POSS-reinforced fluoropolymer.

5   FIG. 8 is a picture of a fluoropolymer showing dispersion of cages at the 1-5 nm level.

6   FIG. 9 shows formation of passivating surface layer upon oxidation of a POSS

7 fluoropolymer.

8   FIG. 10 is an AFM image of 3,3,3-trifluoropropyl$_n$T$_n$ blended into PVDF in 2.94 wt. %.

9 The absence of POSS domains may indicate that the POSS is well dispersed.

10   FIG. 11 is an AFM image of 1H,1H,2H,2H-heptadecafluorodecyl$_n$T$_n$ blended into PVDF

11 in 10 wt. %. The POSS appears to be forming domains within the polymer matrix, indicating

12 that the POSS with a longer fluoroalkyl chain is less soluble in PVDF, or that a 10 wt. % blend is

13 too high for this particular POSS compound. 10% 3,3,3-trifluoropropyl$_n$T$_n$ was blended into

14 PVDF with no domain appearance by AFM.

DEFINITION OF FORMULA REPRESENTATIONS FOR NANOSTRUCTURES

1

2   For the purposes of understanding this invention's chemical compositions the following

3   definitions for formula representations of Polyhedral Oligomeric Silsesquioxane (POSS) and

4   Polyhedral Oligomeric Silicate (POS) nanostructures are made.

5   Polysilsesquioxanes are materials represented by the formula $[RSiO_{1.5}]_\infty$ where ∞

6   represents molar degree of polymerization and R = represents organic substituent (H, siloxy,

7   cyclic or linear aliphatic or aromatic groups that may additionally contain reactive functionalities

8   such as alcohols, esters, amines, ketones, olefins, ethers or halides or which may contain

9   fluorinated groups). Polysilsesquioxanes may be either homoleptic or heteroleptic. Homoleptic

10   systems contain only one type of R group while heteroleptic systems contain more than one type

11   of R group.

12   POSS and POS nanostructure compositions are represented by the formula:

13    $[(RSiO_{1.5})_n]_{\Sigma\#}$ for homoleptic compositions

14    $[(RSiO_{1.5})_n(R'SiO_{1.5})_m]_{\Sigma\#}$ for heteroleptic compositions (where $R \neq R'$)

15    $[(RSiO_{1.5})_n(RXSiO_{1.0})_m]_{\Sigma\#}$ for functionalized heteroleptic compositions (where R groups can

16   be equivalent or inequivalent)

17   In all of the above R is the same as defined above and X includes but is not limited to

18   OH, Cl, Br, I, alkoxide (OR), acetate (OOCR), peroxide (OOR), amine (NR_2) isocyanate (NCO),

19   and R. The symbols m and n refer to the stoichiometry of the composition. The symbol Σ

20   indicates that the composition forms a nanostructure and the symbol # refers to the number of

21   silicon atoms contained within the nanostructure. The value for # is usually the sum of m+n,

22   where n ranges typically from 1 to 24 and m ranges typically from 1 to 12. It should be noted

1   that $\sum\#$ is not to be confused as a multiplier for determining stoichiometry, as it merely describes

2   the overall nanostructural characteristics of the system (aka cage size).

3

4   **DETAILED DESCRIPTION OF THE INVENTION**

5   The present invention teaches the use of nanostructured chemicals as alloying agents for

6   the reinforcement of polymer coils, domains, chains, and segments at the molecular level.

7   The keys that enable nanostructured chemicals to function as molecular level reinforcing

8   and alloying agents are: (1) their unique size with respect to polymer chain dimensions, and (2)

9   their ability to be compatibilized with polymer systems to overcome repulsive forces that

10 promote incompatibility and expulsion of the nanoreinforcing agent by the polymer chains. That

11 is, nanostructured chemicals can be tailored to exhibit preferential affinity/compatibility with

12 some polymer microstructures through variation of the R groups on each nanostructure. At the

13 same time, the nanostructured chemicals can be tailored to be incompatible with other

14 microstructures within the same polymer, thus allowing for selective reinforcement of specific

15 polymer microstructure. Therefore, the factors to effect a selective nanoreinforcement include

16 specific nanosizes of nanostructured chemicals, distributions of nanosizes, and compatabilities

17 and disparities between the nanostrucutured chemical and the polymer system.

18   Nanostructured chemicals, such as the POSS Molecular Silicas illustrated in Figure 3, are

19 available as both solids and oils. Both forms dissolve in molten or in solvents, or directly into

20 polymers thus solving the long-standing dispersion problem associated with traditional

21 particulate fillers or the mixing complexities associated with interpenetrating networks.

22 Moreover, because POSS nanocages dissolve into plastics at the molecular level, the forces (i.e.,

23 free energy) from solvation/mixing are sufficient to prevent POSS from coalescing and forming

1   agglomerated domains as occurs with traditional and other organofunctionalized fillers.

2   Agglomeration of particulate fillers has been a problem that has traditionally plagued formulators

3   and molders.

4   Table 1 below relates the size range of POSS cages relative to polymer dimensions and

5   filler sizes. The size of POSS is roughly equivalent to that of most polymer dimensions, thus at a

6   molecular level POSS can effectively alter the motion of polymer chains.

Particle Type	Particle Diameter
Amorphous Segments	0.5 - 5 nm
Octacyclohexyl POSS	1.5 nm
Random Polymer Coils	5 - 10 nm
Particulate Silica	9 - 80 nm
Crystalline Lamellae	1.0 - 9,000 nm
Fillers / Organoclays	2 - 100,000 nm

7   **Table 1.** Relative sizes of POSS, polymer dimensions, and fillers.

8   The ability of POSS to control chain motion is particularly apparent when POSS is

9   grafted onto a polymer chain. See U.S. Pat. Nos. 5,412,053; 5,484,867; 5,589,562; and

10   5,047,492, all expressly incorporated by reference herein. When POSS nanostructures are

11   covalently linked to the polymer chain they act to retard chain motion and greatly enhance time

12   dependent properties such as T_g, HDT, Creep and Set, which correlate to increased modulus,

13   hardness, and abrasion resistance. The present invention now shows that similar property

1 enhancements can be realized by the direct blending of nanostructured chemicals into plastics.

2 This greatly simplifies the prior art processes.

3   Furthermore, because POSS nanostructured chemicals possess spherical shapes (per

4 single crystal X-ray diffraction studies), like molecular spheres, and because they dissolve, they

5 are also effective at reducing the viscosity of polymer systems. This benefit is similar to what is

6 produced through the incorporation of plasticizers into polymers, yet with the added benefits of

7 reinforcement of the individual polymer chains due to the nanoscopic nature of the chemicals

8 (see Figure 6). Thus ease of processability and reinforcement effects are obtainable through the

9 use of nanostructured chemicals (e.g. POSS, POS) where as prior art would have required the use

10 of both plasticizers and fillers or the covalent linking of POSS to the polymer chains. Additional

11 benefit may be realized by the usage of nanostructured chemicals with monodisperse cage sizes

12 (i.e., polydispersity = 1) or from polydisperse cage sizes. Such control over compatibility,

13 dispersability, and size is unprecedented for all traditional filler, plasticizer, and interpenetrating

14 network technologies.

15

| 1 | EXAMPLES |

2 <u>**General Process Variables Applicable To All Processes**</u>

3   As is typical with chemical processes there are a number of variables that can be used to

4   control the purity, selectivity, rate and mechanism of any process. Variables influencing the

5   process for the incorporation of nanostructured chemicals (e.g. POSS/POS etc.) into plastics

6   include the size and polydispersity, and composition of the nanostructured chemical. Similarly

7   the molecular weight, polydispersity and composition of the polymer system must also be

8   matched with that of the nanostructured chemical. Finally, the kinetics, thermodynamics, and

9   processing aids used during the compounding process are also tools of the trade that can impact

10   the loading level and degree of enhancement resulting from incorporation of nanostructured

11   chemicals into polymers. Blending processes such as melt blending, dry blending and solution

12   mixing blending are all effective at mixing and alloying nanostructured chemical into plastics.

13 <u>**Example 1 - Synthesis**</u>

14   Example 1a

15   (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (6.10 g), deionized water (0.27

16   g), and potassium hydroxide (2.088 mg) were added to a 10 mL volumetric flask. The balance of

17   the volume to 10 mL was filled with ethanol. The contents were transferred to a 25 mL round

18   bottom flask with a Teflon covered magnetic stir bar. The contents were stirred at room

19   temperature overnight under nitrogen. A fine white powder was formed. The product was rinsed

20   with ethanol and dried. A 92.3% yield of pure $[(RSiO_{1.5})_8]_{\Sigma 8})$ was obtained. ^{29}Si NMR δ: -

21   66.76 ppm.

1

2 Example 1b

3   (Tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (5.10 g), deionized water (0.27 g),

4 and potassium hydroxide (2.088 mg) were added to a 10 mL volumetric flask. The balance of

5 the volume to 10 mL was filled with ethanol. The contents were transferred to a 25 mL round

6 bottom flask with a Teflon covered magnetic stir bar. The contents were stirred at room

7 temperature overnight under nitrogen. A fine white powder was formed. The product was rinsed

8 with ethanol and dried. A 92% yield of pure $[(RSiO_{1.5})_8]_{\Sigma 8})$ was obtained. ^{29}Si NMR δ: - 66.69

9 ppm.

10

11 **Example 2- Melt Compounding**

12 Example 2a

13   Poly(vinylidene fluoride) (PVDF) was used. PVDF (Hylar 460) was obtained from

14 Solvay Solexis. The melting temperature determined by differential scanning calorimetry (DSC)

15 was in the range of 150-164 °C. $[(3,3,3\text{-}Trifluoropropyl_nSiO_{1.5})_n]\Sigma_n$ was blended into PVDF

16 using a twin screw extruder (MicroCompounder, DACA Instruments). The PVDF and POSS

17 were mixed thoroughly for 3 minutes at 177 °C. Three samples were prepared with POSS weight

18 percents of 2.5%, 5%, and 10%, respectively.

1   Example 2b

2

3   PVDF was used in this study. $[(1H,1H,2H,2H\text{-heptadecafluorodecyl}_nSiO_{1.5})_n]\Sigma_n$ was

4 blended into PVDF using a twin screw extruder. The PVDF and POSS were mixed thoroughly

5 for 3 minutes at 177 °C. Three samples were prepared with POSS weight percents of 2.5%, 5%,

6 and 10%, respectively.

7

8   Example 2c

9   Perfluoroalkoxy polymer (PFA) was used in this study. PFA was obtained from duPont.

10 The melting temperature determined by DSC was in the range of 311-319 °C. $[(1H,1H,2H,2H\text{-}$

11 $\text{heptadecafluorodecyl}_nSiO_{1.5})_n]\Sigma_n$ was blended into PFA using the twin screw extruder. The PFA

12 and POSS were mixed thoroughly for 3 minutes at 375 °C. Two samples were prepared with

13 POSS weight percents of 2.5% and 10%, respectively.

14

15   Example 2d

16   PFA was used in this study. $[(c\text{-pentyl})SiO_{1.5})_7 \ (c\text{-pentyl})(OH)SiO_{1.0})_3]\Sigma_7$ was blended

17 into PFA using the twin screw extruder. The PFA and POSS were mixed thoroughly for 3

18 minutes at 750 °C. A sample was prepared with a POSS weight percent of 2%.

19

20   Example 2e

21   PFA was used in this study. $[(c\text{-pentyl})SiO_{1.5})_7 \ (H)SiO_{1.5})_3]\Sigma_8$ was blended into PFA

22 using the twin screw extruder. The PFA and POSS were mixed thoroughly for 3 minutes at 750

23 °C. A sample was prepared with a POSS weight percent of 5%.

24   A series of Nanostructured POSS Chemicals were compounded into fluoropolymer at the

25 1wt% - 50wt% level using a twin screw melt extruder operating at 80-120 rpm and 190 °C. Both

1 POSS and the polymer were dried prior to compounding to ensure a maximum state of alloying.

2 After compounding, the POSS-reinforced samples were then molded into discs, dogbones and

3 other test specimens and subjected to analysis and characterization. The viscoelastic response as

4 represented by the values for storage modulus (E*) relative to temperature (°C) of the POSS-

5 reinforced fluoropolymer is shown in Figure 7.

6   Various sizes of POSS molecular silicas were observed to have a pronounced effect on

7 the degree to which the modulus was retained at elevated temperatures. Overall it was observed

8 that the Octameric $[(RSiO_{1.5})_8]\Sigma_8$ and dodecametic $[(RSiO_{1.5})_{12}]\Sigma_{12}$ POSS were most effective at

9 retaining the modulus at elevated temperatures. The fracture toughness and other mechanical

10 properties and physical properties of the POSS-alloyed fluoropolymers were also noticeably

11 improved. The mechanism for this enhancement was observed to be the restriction of the motion

12 of the polymer segments and subsequent polymer chains in the fluoropolymer (see Figure 6). The

13 mechanism erosion resistance in space is attributed to the in situ formation of a passivating

14 glassy surface layer (see Figure 9). Similar levels of enhancement have been observed for other

15 fluoropolymers (e.g. MFA, PFA, PVDF, TFE, etc.).

16 **Alternate Method: Solvent Assisted Formulation.** POSS can be added to a vessel containing

17 the desired polymer, prepolymer or monomers and dissolved in a sufficient amount of an organic

18 solvent (e.g. hexane, toluene, dichlormethane, etc.) or fluorinated solvent to effect the formation

19 of one homogeneous phase. The mixture is then stirred under high shear at sufficient

20 temperature to ensure adequate mixing for 30 minutes and the volatile solvent is then removed

21 and recovered under vacuum or using a similar type of process including distillation. Note that

22 supercritical fluids such as CO_2 can also be utilized as a replacement for the flammable

23 hydrocarbon solvents. The resulting formulation may then be used directly or for subsequent

1   processing.

2   **Example 3 - Incorporation into fluorinated fluids**

3   Nanostructured POSS was compounded into fluoropolymer fluids in the amounts ranging

4   from 1%, to 50%, and various physical properties of the alloyed fluids were measured and

5   compared with the same physical properties of the base fluorpolymer fluid (Table 3). The

6   enhanced properties of POSS-reinforced fluoropolymer fluid are apparent. Similar levels of

7   enhancements were observed with other fluoro polymer fluids and from the incorporation of

8   POSS fluoropolymer fluids into other polymers.

9   The mechanism for the physical property enhancements is attributed to the restriction of

10   motion of the polymer chains (see Figure 6). The mechanism erosion resistance in space is

11   attributed to the in situ formation of a passivating glassy surface layer (see Figure 9).

12   **Example 4**

13   A transmission electron micrograph was taken of a fractured POSS fluoropolymer

14   monolith of that was composed of 10% $[(RSiO_{1.5})_8]_{\Sigma 8}$) (see Figure 8), which illustrates the

15   molecular level dispersion that can be achieved in polymers via compounding. Specifically, the

16   black dots in Figure 8 represent POSS molecular silica dispersed at the 1 nm to 3 nm level.

17   What is claimed: